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Study on pH in water and potassium chloride for Bulgarian soils

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Abstract

Soil pH is commonly measured in water $pH(H_2O)$ or $pH(KCl)$. The relationship between $pH(H_2O)$ and $pH(KCl)$ across all Bulgarian soils were investigated and results examining the effect of soil type on the relationship were presented. Several functions were used to estimate dependence between the two measures. For all soils and depths, a linear regression accounted for 95.32% of the variation, which predicts $pH(KCl)$ very well. From the analysis of data follows that they were differentiated into three clusters.

Keywords: Soil pH, soil database, cluster analysis.

Introduction

Study on pH measured by different methods are in progress in different countries such as: Romania (Gavriloaei, 2012), Australia (Ahem et al. 1995; Minasny et al., 2011), Poland (Kabała et al., 2016). Unfortunately, there are several measures of soil reaction used worldwide. The most common extracts are distilled water (H_2O), 1 mol L^{-1} KCl (KCl), and 0.01 mol L^{-1} $CaCl_2$ ($CaCl_2$). Different measurement methods lead, however, to incompatibility of data from various countries and disturb data integration in the international soil databases.

In this article the relationship between $pH(H_2O)$ and $pH(KCl)$ across all Bulgarian soils were investigated and results examining the effect of soil type on this relationship were presented. For all soils and depths, several regression equations were calculated, which predicts $pH(KCl)$ in dependence of $pH(H_2O)$. The study was intended to help scientists and practitioners in using both methods of pH when dealing with problems of liming of acidic soils.

Material and Methods

Since 1956 the data from the large-scale soil survey have been used to compile soil maps of Bulgarian geographical regions at different scale. Thematic maps of the whole of Bulgaria have been prepared also to facilitate the soil agro-ecological partition at a scale of 1:600,000 (Yolevski et al., 1980), land evaluation for crop production at 1:1,000,000 scale (Kabakchiev et al., 1985). Until that time the so-called agro-ecological grouping of soils was adopted for the needs of agriculture. In Table 1 the total areas and arable areas are presented.

The materials of the study are the values of $pH(H_2O)$ and $pH(KCl)$ given in Reference database for soils in Bulgaria (Teoharov et al., 2009). This valuable source contains 306 data from different soils, namely: Chernozems (64), Gray Forest soils (33), Pseudopodzolic Forest soils (54), Cinnamonic Forest soils (33), Zheltozem soils (30), Leached Smolnitsa (15), Brown Forest soils (11), Mountainous Meadow soils (3), Alluvial Meadow soils (21), Peat-gley soils (11), Rankers (21), Regosols (9), Rendzinas (2), and Technogenic soils (17).

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Table 1. Agro-ecological groups of the total and arable area (Yolevski, 1986).

Code	Agro-ecological groups	Total area		Arable area	
		1000 ha	(%)	1000 ha	(%)
01	Calcareous and typical chernozems	1047.25	9.435	444.04	16.332
02	Leached chernozems	967.29	8.714	410.13	13.965
03	Podzolic chernozems and dark gray forest soils	538.62	4.852	228.37	5.598
04	Gray forest soils	1158.31	10.435	491.12	11.657
05	Light gray pseudopodzolic forest soils	577.49	5.203	244.86	3.742
06	Smolnitsa soils	659.67	5.943	279.70	8.698
07	Cinnamonic forest soils	2037.87	18.359	864.06	14.617
08	Cinnamonic podzolic forest soils	928.42	8.364	393.65	4.374
09	Brown forest soils	1910.16	17.209	809.91	2.909
10	Meadow soils	999.50	9.005	423.79	16.653
11	Rendzinas (humus-carbonate soils)	275.42	2.481	116.78	1.455
	Sum	11100.00	100.00	4706.40	100.00

Preliminary check of the data shows that three points were erroneous (Chernozem profile No. 32/3/C1k and C2k; Gray Forest profile No. 8 B2t) and were excluded from the analysis. The Technogenic soils also have been excluded. So we had 304 pairs for analysis. First step was performing descriptive statistical analysis. Results are given in Table 2 and 3.

Table 2. Statistical characteristics of different soils.

Soil	Variable	Valid N	Mean	Median	Std.Dev.	Minimum	Maximum	Skewness	Kurtosis
Chernozems	H_2O	62	7.4403	7.75	0.7221	6.00	8.30	-0.686	-0.945
	KCl	62	6.6226	7.10	0.9510	4.60	7.80	-0.725	-0.897
Gray Forest	H_2O	32	6.2531	5.50	1.2324	4.30	8.20	0.541	-1.307
	KCl	32	5.2922	4.70	1.2422	3.40	7.40	0.524	-1.333
Pseudopozolic Forest	H_2O	54	5.3796	4.85	1.1690	4.00	8.40	1.209	0.269
	KCl	54	4.3287	3.85	1.2783	2.90	7.20	1.174	0.044
Cinnamonic Forest	H_2O	32	7.0500	7.70	1.1188	4.70	8.20	-1.049	-0.249
	KCl	32	6.1016	6.80	1.2652	3.40	7.40	-1.048	-0.219
Zheltozem	H_2O	30	4.9300	4.90	0.2818	4.40	5.90	1.322	4.224
	KCl	30	3.8017	3.75	0.3865	3.20	4.95	1.489	2.905
Leached Smolnitsa	H_2O	15	6.9867	7.10	0.7130	6.10	8.20	0.332	-1.095
	KCl	15	5.9933	5.90	0.7363	5.10	7.20	0.377	-1.329
Brown Forest	H_2O	11	5.4864	5.40	1.1845	4.00	7.20	0.074	-1.640
	KCl	11	4.4055	4.40	1.0340	3.10	5.90	0.067	-1.667
Alluvial Meadow	H_2O	21	7.6810	8.10	0.6853	5.80	8.30	-1.236	1.135
	KCl	21	7.0714	7.50	0.8113	5.40	7.80	-1.104	-0.246
Peat-gley	H_2O	11	7.5727	7.70	0.4052	6.80	8.00	-0.839	-0.493
	KCl	11	7.0727	7.10	0.2687	6.50	7.40	-0.818	0.757
Rankers	H_2O	21	4.9643	4.95	0.5730	4.10	6.20	0.035	-0.418
	KCl	21	4.2333	4.20	0.6187	3.10	5.50	0.217	-0.500
Regosols	H_2O	9	7.9333	8.00	0.5745	6.70	8.60	-1.275	1.873
	KCl	9	6.8556	6.90	0.6002	5.60	7.50	-1.139	1.301

Table 3. Descriptive statistics from combined analysis of pH(H_2O) and pH(KCl).

pH	N	Mean	Median	Std.Dev.	Min	Max	Skewness	Kurtosis
H_2O	304	6.4158	6.45	1.3879	4.00	8.60	-0.095	-1.519
KCl	304	5.4976	5.50	1.5262	2.90	7.80	-0.047	-1.528

There is another collection of data with the properties of soils in Bulgaria (Ninov et al., 1975). Unfortunately, it is too limited and not all pH analyzes by both methods are included simultaneously for different soils.

Next step was performing regression analysis to describe the link between pH(H_2O) and pH(KCl). The aim was to find the most appropriate function, which accurately describes the relationship between the values of both pH analyzes. It was also interesting to investigate the distribution of pH and its differentiation across the different soil groups. For this purpose cluster analysis was applied.

We are looking for a regression of the type

$$y = f(x),$$

where $y = $ pH(KCl), $x = $ pH(H$_2$O) and f is a selected regression model.

We consider the following types of equations:

(a) $\quad y = a + bx,$ Linear function

(b) $\quad y = a + bx + cx^2,$ Quadratic function

(c) $\quad y = \dfrac{1}{a + bx + cx^2},$ Reciprocal Quadratic function

(d) $\quad y = ab^x x^c,$ Hoerl function

Selected function have no more than three parameters to be estimated. The principle of Ocam is followed: "Of two competing theories, the simpler explanation of an entity is to be preferred" (Duignan, 2017). If you have a few hypotheses that could explain an observation, it is usually best to start with the simplest one.

Results and Discussion

The United States Department of Agriculture, formerly Soil Conservation Service (Soil Survey Staff, 1993) classifies soil pH in water ranges as follows in Table 4. FAO classification applicable in Bulgaria is given in (Gyurov and Artinova, 2015).

Table 4. pH classification by USA and FAO (applicable in Bulgaria).

USA accepted classification		FAO accepted classification	
Denomination	pH range	pH(H$_2$O)	Reaction
Ultra acid	< 3.5	< 3.0	Extremely acid
Extremely acid	3.5–4.4	3.0-4.0	Very strongly acid
Very strongly acid	4.5–5.0	4.1-5.0	Strongly acid
Strongly acid	5.1–5.5	5.1-6.0	Moderately acid
Moderately acid	5.6–6.0	6.1-6.9	Slightly acid
Slightly acid	6.1–6.5	7.0	Neutral
Neutral	6.6–7.3	7.1-7.5	Very slightly alkaline
Slightly alkaline	7.4–7.8	7.6-8.1	Slightly alkaline
Moderately alkaline	7.9–8.4	8.2-8.6	Moderately alkaline
Strongly alkaline	8.5–9.0	8.7-8.9	Alkaline
Very strongly alkaline	> 9.0	9.0-10.0	Strongly alkaline
		10.1-11.0	Very strongly alkaline

First, for each of the soils all models (a), (b), (c) and (d) are calculated. Results of corresponding correlation coefficients R^2 are presented in Table 5. Because of their small numbers of data Mountainous Meadow soils and Rendzinas are excluded from separate consideration, but they are included in the combined analysis.

Table 5. Values of correlation coefficients R^2 of models for different soils.

Soils	N	Models			
		(a)	(b)	(c)	(d)
Chernozems	62	0.9078	0.9174	0.9206	0.9183
Gray Forest soils	32	0.9291	0.9291	0.9299	0.9292
Pseudopodzolic Forest soils	54	0.9623	0.9636	0.9660	0.9634
Cinnamonic Forest soils	33	0.9786	0.9786	0.9791	0.9786
Zheltozem soils	30	0.9152	0.9161	0.9176	0.9161
Leached Smolnitsa	15	0.9060	0.9080	0.9082	0.9081
Brown Forest soils	11	0.9884	0.9884	0.9893	0.9884
Alluvial Meadow soils	21	0.9298	0.9328	0.9328	0.9323
Peat-gley soils	11	0.8008	0.8597	0.8600	0.8596
Rankers	21	0.8438	0.8439	0.8424	0.8438
Regosols	9	0.9945	0.9943	0.9949	0.9948

Types of models: (a) Linear function, (b) Quadratic function, (c) Reciprocal Quadratic function, (d) Hoerl function.

It is evident that the highest values of R^2 are for the model (c) Reciprocal Quadratic function in almost all soils. But let's not rush to the conclusions about the most suitable function before looking at combined data and applying Ocam's principle.

In the analysis of all 304 value pairs, the following regressions are obtained,

where y = pH(KCl) and x = pH(H$_2$O):

(a) $$y = a + bx,$$ a = -1.39116 b = 1.07371 R^2 = 0.9533

(b) $$y = a + bx + cx^2,$$ a = -0.38044 b = 0.73943 c = 0.02632 R^2 = 0.9766

(c) $$y = \frac{1}{a + bx + cx^2},$$ a = 0.72916 b = -0.13037 c = 0.0006526 R^2 = 0.9776

(d) $$y = ab^x x^c,$$ a = 0.49694 b = 0.99356 c = 1.31154 R^2 = 0.9767

If you follow the Ocam's principle, it is natural to accept the linear regression, which has only two coefficients:

pH(KCl) = -1.39116 + 1.07371 × pH(H$_2$O) with R^2 = 0.9533.

The R-Squared statistic indicates that the model as fitted explains 95.33% of the variability in pH(KCl). The adjusted R-squared statistic, which is more suitable for comparing models with different numbers of independent variables, is 95.32%. The standard error of the estimate shows the standard deviation of the residuals to be 0.33029. This value can be used to construct prediction limits for new observations.

If available data for pH are analyzed with KCl, it can be used the reverse analysis, where y = pH(H$_2$O), x = pH(KCl) and gives the equation:

pH(H$_2$O) = 1.53466 + 0.88787 × pH(KCl) with R^2 = 0.9533.

It should not be forgotten that the analyzes of both methods - in water and potassium chloride, produce results with a certain error. It is logical to use the orthogonal regression method (Total least squares), which is appropriate in such case. That gives the equation:

pH(KCl) = -0.076319 + 0.86878 × pH(H$_2$O) with R^2 = 0.9536.

It should be noted that this method gives the same average value of the dataset, but with a smaller standard error equal to 1.2057. Figure 1 shows the straight lines of linear and orthogonal regression.
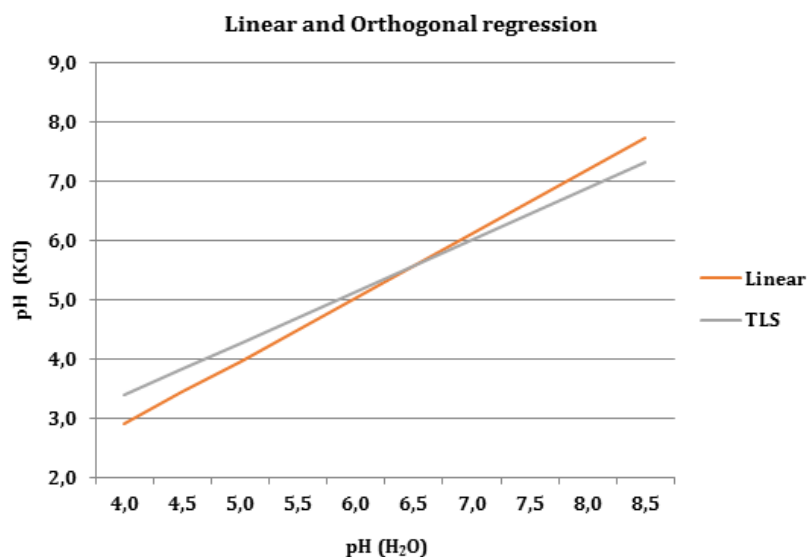

Figure 1. Both regression lines.

It is interesting to see the histograms of the distributions of the two variables.
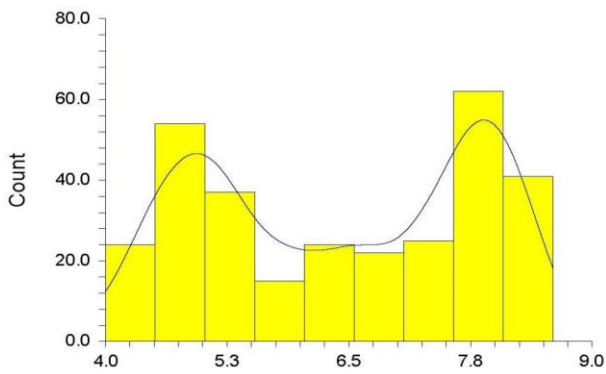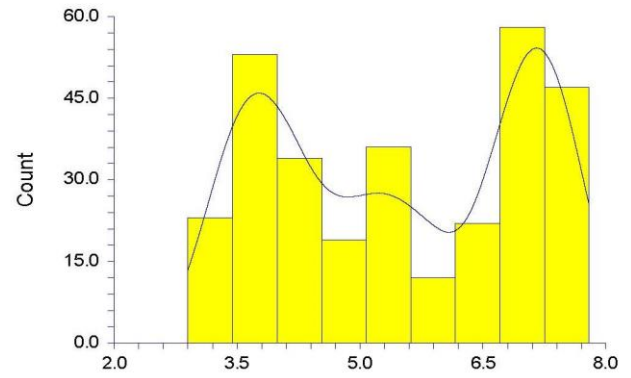
Figure 2. Histogram of pH(H$_2$O)

Figure 3. Histogram of pH(KCl)

Obviously, it differs significantly from Normal (Gaussian) distribution and is a mixture of two or more different distributions. This justifies the use of cluster analysis to identify the groups that determine the differences in analyses. As a result of this analysis, three clusters were obtained, the statistical characteristics of which are given in Table 6.

Table 6. Statistical characteristics of three Clusters.

	pH	N	Mean	Median	St. Dev.	Min	Max	Skewness	Kurtosis
Cluster 1	H$_2$O	123	7.8728	7.90	0.3343	6.80	8.60	-0.470	0.208
	KCl	123	7.1305	7.20	0.3612	6.30	7.80	-0.311	-0.447
Cluster 2	H$_2$O	62	6.4565	6.40	0.4344	5.40	7.20	-0.095	-0.741
	KCl	62	5.4387	5.45	0.4112	4.60	6.30	0.100	-0.264
Cluster 3	H$_2$O	119	4.8887	4.90	0.4090	4.00	5.60	-0.171	-0.620
	KCl	119	3.8404	3.80	0.4563	2.90	4.90	0.294	-0.562

Closer examination of the data shows the following:

- Members of Cluster 1 are predominantly data from Alluvial Meadow soils, Chernozems and Gray Forest soils. Hypothesis for Normal distribution can't be confirmed.

- Members of Cluster 2 are data from Chernozems, Brown Forest soils and Leached Smolnitsa. Hypothesis for Normal distribution can't be rejected.

- Members of Cluster 3 are data from Pseudopodzolic Forest soils, Rankers and Zheltozem soils. Hypothesis for Normal distribution can't be rejected.

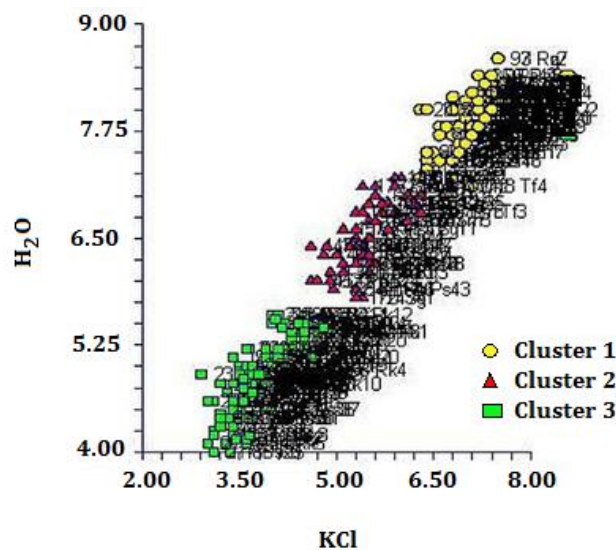Figure 4 shows a distinct differentiation between the three clusters.

Figure 4. Cluster analysis

The presence of objects from the same soil group as members of different clusters can be explained by the large soil diversity in Bulgaria and some inaccuracies in the identification of soil profiles.

The simple linear model equation (a) seems to perform very well and is almost accurate as the nonlinear models equations (b, c, d) across all the datasets. As a result, values of pH in KCl can be predict as a function of pH in water and vice versa. From a purely statistical point of view, it is advisable to use orthogonal linear regression, which takes into account the fact that in both methods the results are obtained with a certain error.

Conclusion

The analysis of 304 pairs results from soil samples is the basis for reliable conclusions. The results of this study allow soil reaction data obtained from different methods - with distilled water (H_2O) and 1 mol L^{-1} KCl (KCl), to be converted and integrate into national and international soil databases. The difference between pH in water and pH in KCl is that the first refers to the acidity of the soil solution, while the pH in KCl refers to the acidity of the soil solution plus the reserve acidity in the colloids and therefore it is always more acid than pH in water. Regression between $pH(H_2O)$ and $pH(KCl)$ is important because it gives the possibility for soil scientists to directly compare own values with the data already existing in literature from other country.

Monitoring pH changes over time is an important management tool. By comparing past and present soil tests, it is possible to see if the soil acidity is increasing over time and, if it is, to alter management methods to prevent this trend from continuing. Analysis of the results from the soil survey in Bulgaria shows that almost half of the soil resources are vulnerable to anthropogenic acidification. Special attention must be paid to genetically acid soils under cultivation. Their additional acid loading has to be controlled to avoid anthropogenic soil degradation.

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